Estimating the density scaling exponent of viscous liquids from specific heat and bulk modulus data

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It was recently shown by computer simulations that a large class of liquids exhibits strong correlations in their thermal fluctuations of virial and potential energy [Pedersen *et al.*, Phys. Rev. Lett. **100**, 015701 (2008)]. Among organic liquids the class of strongly correlating liquids includes van der Waals liquids, but excludes ionic and hydrogen-bonding liquids. The present note focuses on the density scaling of strongly correlating liquids, i.e., the fact their relaxation time τ at different densities ρ and temperatures T collapses to a master curve according to the expression $\tau \propto F[\rho^\gamma/T]$ [Schrøder *et al.*, arXiv:0803.2199]. We here show how to calculate the exponent γ from bulk modulus and specific heat data, either measured as functions of frequency in the metastable liquid or extrapolated from the glass and liquid phases to a common temperature (close to the glass transition temperature). Thus an exponent defined from the response to highly nonlinear parameter changes may be determined from linear response measurements.

Introduction

A liquid is termed "strongly correlating" if its viral (W) and potential energy (U) equilibrium fluctuations correlate better than 90% [2, 3, 10] at constant volume and temperature,

$$\Delta W(t) \cong \gamma \Delta U(t). \tag{1}$$

where $\Delta W(t) = W(t) - \langle W \rangle$, $\Delta U(t) = U(t) - \langle U \rangle$. The "slope" is defined as

$$\gamma \equiv \sqrt{\frac{\langle (\Delta W)^2 \rangle}{\langle (\Delta U)^2 \rangle}} \tag{2}$$

and the correlation coefficient is defined as

$$R \equiv \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}}. \tag{3}$$

We have previously shown that the fluctuations of such liquids are well described by those generated by soft-sphere potentials (inverse power law potentials) [2, 3]. Strongly correlating liquids are approximate single-parameter liquids [1, 6, 11]. Moreover the density scaling exponent is one third of the exponent of the approximate inverse power law potentials [5, 14]. Recall that density (thermodynamic) scaling applies whenever the relaxation time τ at different densities ρ and temperatures T collapse to a master curve according to the expression $\tau \propto F[\rho^\gamma/T]$. It is generally reported now that density scaling applies for van der Waals liquids, but e.g. not for hydrogen-bonding liquids. This is consistent with our finding that the class of strongly correlating liquids includes van der Waals and metallic liquids, but excludes covalent, ionic, or hydrogen-bonding liquids – the latter three classes of liquids have competing interactions that spoil the WU correlation [2, 3, 10].

Fluctuation expressions

Consider a viscous liquid with slow structural relaxation, i.e., with a relaxation time τ that is much larger than one picosecond. The fluctuation-dissipation (FD) theorem for the frequency-dependent specific heat per unit volume, $c_V(\omega)$, is given [9] by

$$k_B T^2 V \, c_V(\omega) \, = \, \langle (\Delta E)^2 \rangle - i\omega \int_0^\infty \langle \Delta E(0) \Delta E(t) \rangle e^{-i\omega t} dt \, . \tag{4}$$

Relaxation takes place over a limited range of frequencies – typically 3-5 decades. By subtracting the responses at high ("∞") and low ("0") frequencies well outside the relaxation frequency range, it follows that if t_s is a time much shorter than those of the relaxations, but much longer than one picosecond, then

$$k_B T^2 V\ (c_V(0) - c_V(\infty))\ =\ \langle \Delta E(0) \Delta E(t_s) \rangle\,. \tag{5}$$

Write the energy as potential plus kinetic energy, $E = U + K$. Because the kinetic energy in the NVT ensemble fluctuates fast compared to t_s one has $\langle \Delta E(0) \Delta E(t_s) \rangle \cong \langle \Delta U(0) \Delta U(t_s) \rangle$. Thus,

$$k_B T^2 V\ (c_V(0) - c_V(\infty))\ =\ \langle (\Delta U)^2 \rangle^{\rm slow} \tag{6}$$

where $\langle (\Delta U)^2 \rangle^{\rm slow} = \langle \Delta U(0) \Delta U(t_s) \rangle$ is the slow part of the potential energy fluctuations, i.e., slow compared to the picosecond time scale.

Since the low-frequency limit gives the ordinary (dc) liquid specific heat and the high-frequency limit gives the "glassy" specific heat corresponding to perturbations that probe a frozen structure, this result may be written

$$\langle (\Delta U)^2 \rangle^{\rm slow} = k_B T^2 V (c_V^{\rm liquid} - c_V^{\rm solid})\,. \tag{7}$$

Similarly one finds for the virial fluctuations (where K_T is the isothermal bulk modulus)

$$\langle (\Delta W)^2 \rangle^{\rm slow}\ =\ -\,k_B T V (K_T^{\rm liquid} - K_T^{\rm solid}) \tag{8}$$

and for the virial / potential energy correlation (where β is the pressure coefficient)

$$\langle \Delta W \Delta U \rangle^{\rm slow} = k_B T^2 V (\beta_V^{\rm liquid} - \beta_V^{\rm solid})\,. \tag{9}$$

Calculating R and γ from data

The WU correlation coefficient (Eq. 3) on the t_s timescale can now be expressed in terms of experimental linear response quantities as follows:

$$R = \frac{(\beta_V^{\rm liquid} - \beta_V^{\rm solid})}{\sqrt{-(K_T^{\rm liquid} - K_T^{\rm solid})(c_V^{\rm liquid} - c_V^{\rm solid})/T}}\,. \tag{10}$$

Similarly the slope (Eq. 2) can be calculated as

$$\gamma = \sqrt{\frac{-(K_T^{\rm liquid} - K_T^{\rm solid})}{T(c_V^{\rm liquid} - c_V^{\rm solid})}}. \tag{11}$$

Calculating γ for the commercial silicone oil DC704

The slope γ may be estimated from the high- and low-frequency limits of $c_p(\omega)$ and $K_S(\omega)$ (and a rough estimate of α_p) by proceeding as follows. Recall the identities

$$c_V = c_p - T\alpha_p^2 K_T \tag{12}$$

and

$$K_T = K_S \frac{c_V}{c_p}. \tag{13}$$

Combining these we get

TABLE I: γ of DC704 data of from the high and low frequency limit of $c_p(\omega)$ and $K_S(\omega)$ [7]. [a] α_p^{solid} is estimated as a typical value of solids.

T [K]	214
c_p^{liquid} [10^6 J/(K m^3)]	1.40
c_p^{solid} [10^6 J/(K m^3)]	1.05
K_S^{liquid} [10^9 Pa]	3.6
K_S^{solid} [10^9 Pa]	5.1
α_p^{liquid} [10^{-3} K^{-1}]	0.5
α_p^{solid} [10^{-3} K^{-1}]	0.1[a]
$T(\alpha_p^{\text{liquid}})^2 K_S^{\text{liquid}}/c_p^{\text{liquid}}$	0.13
$T(\alpha_p^{\text{solid}})^2 K_S^{\text{solid}}/c_p^{\text{solid}}$	0.01
c_V^{liquid} [10^6 J/(K m^3)]	1.24
c_V^{solid} [10^6 J/(K m^3)]	1.04
K_T^{liquid} [10^9 Pa]	3.1
K_T^{solid} [10^9 Pa]	5.0
γ (Eq. 11)	6

$$c_V = c_p \left(1 + \frac{T\alpha_p^2 K_S}{c_p}\right)^{-1}, \tag{14}$$

and

$$K_T = K_S \left(1 + \frac{T\alpha_p^2 K_S}{c_p}\right)^{-1}. \tag{15}$$

The value $\gamma = 6$ is calculated from these expressions using our unpublished linear response data (table I). Unfortunately no experimental density scaling γ's are available for this liquid to compare to.

OTP/OPP mixture and pure OTP

The high- and low-frequency limits of the dynamic response can be estimated by extrapolation of static response functions of the glass and liquid phases to a temperature close to the glass transition temperature T_g. Table II lists extrapolated values of κ_T, c_p and α_p for a mixture of o-terphenyl (OTP) and o-phenylphenol (OPP), Table III lists values for pure OTP.

From the natural response functions of the constant pT ensemble it is straightforward to calculate the natural response functions of the constant VT ensemble:

$$K_T = 1/\kappa_T, \tag{16}$$

$$c_V = c_p - T\alpha_p^2 K_T, \tag{17}$$

and

$$\beta_V = \alpha_p K_T. \tag{18}$$

Using these equations we arrive at the numbers in tables II and III.

TABLE II: γ and R of OTP-OPP calculated from data on Figure 4 of Ref. [15]

T_g [K]	233.7
V_g [10^{-6}m^3/mol]	203.9
$C_p^{\rm liquid}$ [J/(K mol)]	364
$C_p^{\rm solid}$ [J/(K mol)]	236
$\kappa_T^{\rm liquid}$ [10^{-9} Pa^{-1}]	0.35
$\kappa_T^{\rm solid}$ [10^{-9} Pa^{-1}]	0.19
$\alpha_p^{\rm liquid}$ [10^{-3} K^{-1}]	0.74
$\alpha_p^{\rm solid}$ [10^{-3} K^{-1}]	0.17
$C_V^{\rm liquid}$ [J/(K mol)]	284
$C_V^{\rm solid}$ [J/(K mol)]	229
$K_T^{\rm liquid}$ [10^9 Pa]	2.9
$K_T^{\rm solid}$ [10^9 Pa]	5.2
$\beta_V^{\rm liquid}$ [10^6 Pa/K]	2.1
$\beta_V^{\rm solid}$ [10^6 Pa/K]	0.9
R (Eq. 10)	0.8
γ (Eq. 11)	6.0
$\gamma^{\rm scale}$ (Ref. [13])	6.2

TABLE III: γ and R for OTP. C_p values are from Ref. [4]. $K_T = \beta_V/\alpha_p$ is calculated from α_p and β_V values from Ref. [8].

T_g [K]	244.5
V_g [10^{-6}m^3/mol]	206.1
$C_p^{\rm liquid}$ [J/(K mol)]	336
$C_p^{\rm solid}$ [J/(K mol)]	228
$\alpha_p^{\rm liquid}$ [10^{-3} K^{-1}]	0.71
$\alpha_p^{\rm solid}$ [10^{-3} K^{-1}]	0.32
$\beta_V^{\rm liquid}$ [10^6 Pa/K]	1.56
$\beta_V^{\rm solid}$ [10^6 Pa/K]	1.16
$C_V^{\rm liquid}$ [J/(K mol)]	280
$C_V^{\rm solid}$ [J/(K mol)]	209
$K_T^{\rm liquid}$ [10^9 Pa]	2.2
$K_T^{\rm solid}$ [10^9 Pa]	3.6
R (Eq. 10)	0.3
γ (Eq. 11)	4.1
$\gamma^{\rm scale}$ (Ref. [13])	4.0

Summary

We have shown that it is possible to calculate the density scaling exponent γ from linear response measurements of specific heat and bulk modulus data. There are two ways to do this: Either by measuring broad-range frequency-dependent linear responses in the equilibrium metastable liquid phase or by extrapolations as done when evaluating the Prigogine-Defay ratio [12]. Using the first method for DC704 we find $\gamma = 6$. To the best of our knowledge there are yet no density scaling data for this liquid. Using the second method for the OTP-OPP mixture we find $\gamma = 6.0$ which compares favorably to the density scaling $\gamma^{\rm scale} = 6.2$ [13]; similarly we find $\gamma = 4.1$ for pure OTP that compares favorably to the density scaling $\gamma^{\rm scale} = 4.0$ [13]. This good agreement may well be fortuitous given the uncertainties associated with our γ estimates. Nevertheless these preliminary findings suggest that for strongly correlating liquids ("single-parameter liquids") the density scaling exponent – which refers to highly nonlinear parameter changes – may

be determined from linear response measurements. This is consistent with a general hypothesis of ours that strongly correlating liquids have simpler physics than liquids in general.

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